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(71) Applicant (*for all designated States except US*): CARA PLASTICS INC. [US/US]; Newark, DE 19711 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): KUSEFOGLU, Selim [TR/TR]; Koybasi Coa, 336–C3 Venikoy, Istanbul (TR). PALMESE, Guiseppe [US/US]; 113 Wooden Carriage Drive, Hockessin, DE 19707 (US). KHOT, Shrikant [US/US]; 808 Waters Edge Drive, Newark, DE 19702 (US). ZHAO, Ralph [US/US]; 22–2A Fairway Road, Newark, DE 19711 (US). WOOL, Richard [US/US]; 208 Orchard Road, Newark, DE 19711 (US).

(74) Agent: PEZZNER, Ashley, L; Connolly & Hutz, 1220 Market Street, Wilmington, DE 19899 (US).

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(54) Title: HIGH MODULUS POLYMERS AND COMPOSITES FROM PLANT OILS

(57) Abstract

The liquid resins described herein are derived from plant and animal oil triglycerides by suitably functionalizing the triglyceride with chemical groups that render it polymerizable. The triglyceride molecular structure is a combination of various triesters of fatty acids linked together with glycerol. The fatty acid residues are linear carboxylic acids containing from about 4 to about 30 carbon atoms, but preferably from about 14 to about 22 carbons and from about zero to about 4, or preferably from about 2 to 3 carbon–carbon double bonds. As obtained in nature, these double bonds are predominantly in the cis (Z) configuration and, in the case of polyunsaturated acids, not conjugated. The fatty acids derived from triglycerides include, but are not limited to the following: Lauric (C12:0), i.e., 12 carbon atoms long containing zero C=C double bonds, Myristic (C14:0), Palmitic (C16:0), Stearic (C18:0), Oleic (C18:1), Linoleic (C18:2), Linolenic (C18:3), Eicosanoic (C20:0), cis–11–Eicosanoic (C20:1), Docosanoic (C22:0) and cis–13–Docosanoic (C22:1). Typical plant oil triglycerides used for the purpose of this invention contain about 10–20 % saturated, about 20–30 % mono–unsaturated, about 40–60 % di–unsaturated, and about 5–15 % tri–unsaturated fatty acid residues, but other distributions, both narrow and broad, of fatty acid residues can also be used for the thermoset and plastic resins described in this invention.

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HIGH MODULUS POLYMERS AND COMPOSITES FROM PLANT OILS

FIELD OF THE INVENTION:

This invention refers to the synthesis and application of liquid resins derived predominantly from plant triglycerides as raw materials, that are capable of curing to high modulus thermosetting polymers suitable for use alone or as the matrix polymer in fiber reinforced composites.

BACKGROUND OF THE INVENTION

Polymer Matrix Composites (PMC) are manufactured by embedding strong fibers such as, glass, carbon, aramid or natural fibers in a polymer. The composite materials benefit from the reinforcement provided by the strong fibers and have tensile, bending and impact strength properties much higher than non-reinforced polymers. Such composites find use in agricultural equipment, civil and marine infrastructure, automotive, construction materials, aircraft and military industries. The polymer used in the composite, also known as the matrix, may be thermoplastic or thermosetting. Thermoplastic polymers are capable of melting upon heating with no change in chemical structure, whereas, thermosetting polymers are capable of chemically reacting. This converts the original, usually liquid, polymer to a rigid solid polymer that can no longer melt upon heating. The latter thermosetting polymers are used as liquid molding resins, successful examples of which include, but are not limited to, the well known unsaturated polyester, vinyl ester and epoxy resins. These resins are usually injected as a liquid into a mold containing the appropriate reinforcing fiber and are then cured in the mold to a rigid solid by the action of heat and catalyst. The successful liquid molding resins must have a low initial viscosity, have a long shelf life at room temperature, be capable of chemically reacting t a solid polymer by

heating and/or addition of catalysts, must be able to react without the formation of volatile by-products, must have strong adhesion to the fibers used as the reinforcing agent and must have good physical properties such as, high ultimate tensile strength, fatigue resistance, impact strength, bending moment and high softening temperature.

Liquid molding resins are usually prepared by first synthesizing a low molecular weight polymer having the functional groups required for the cross-linking reaction. To achieve the desired low viscosity the polymer may be dissolved in a reactive diluent. If the cross-linking reaction is of the free radical addition type, the required functional group on the polymer is ethylenic unsaturation and the reactive diluent is also an ethylenicly unsaturated compound such as, but not limited to, styrene, α-methyl styrene, divinyl benzene, methyl methacrylate, etc. The relative ratios of unsaturated groups on the polymer and the amount of the reactive diluent are important parameters that those knowledgeable in the field have learned to optimize.

Just prior to use, liquid molding resins are mixed with catalysts and accelerators that start and facilitate the cross-linking reaction. If the cross-linking reaction is of the addition type, such accelerators as cobalt naphtenate, aromatic tertiary amines, etc., and free radical initiators such as, but not limited to, methyl ethyl ketone peroxide, benzoyl peroxide, cumyl hydroperoxide , etc., are added. The choice of initiators and accelerators depends on the reactivity of the polymer and the temperature and the time desired for the cure reaction. The choice of accelerators and initiators are well documented in the literature and are well known by those experienced in this field.

Successful liquid moldings such as, but not limited to, unsaturated polyesters, vinyl esters and epoxy resins are all synthesized using raw materials derived ultimately from petroleum. These include, but are not limited to, maleic anhydride, phthalic acid, isophthalic acid, aliphatic diols, bisphenol-A, acrylic and methacrylic acid, aliphatic and aromatic diamines, all of which are petroleum derivatives. Replacing some, or all, of these petroleum derived raw materials with renewable plant-based raw materials is attractive, both economically and socially, as such raw materials are cheaper and their use contributes to global sustainability by not depleting scarce resources.

The use of plant-based raw materials such as plant oils is further useful as such

naturally occurring compounds are usually consumed readily by microorganisms. In fact, plant triglycerides are readily hydrolyzed in vivo by lipase secreting bacteria. This would make polymers derived from such raw materials easily biodegradable in natural media. This aspect of these polymers is an additional advantage over polymers derived solely from petroleum based raw materials, very few of which are degradable by naturally occurring bacteria.

It is also the intention of the present invention to introduce a high modulus resin system that is suitable for composite formation using man made fibers such as, glass, carbon and aramid fibers as well as natural fibers, including, but not limited to, animal fiber (e.g., wool, cashmere, hair, bird feathers, etc.), and plant or vegetable fiber (cotton, sisal, fibrous cellulose, hemp, hay, straw, flax, jute, pine needles, etc.). In this manner, it is intended to produce composites whose matrix as well as reinforcement are predominantly made from natural and renewable materials. These materials are inexpensive and should find use in high volume applications such as, but not limited to, particle board for furniture and construction, engineered lumber, reinforced components for automotive, OFB and MDF panels for construction, ceiling panels and sculpture. By controlling the crosslink density, these materials are suited to applications as softer, low modulus materials such as rubber and flexible composites

The use of epoxidized triglycerides, especially epoxidized soybean oil, is well documented. This compound is available in many levels of epoxidation and for the purposes of this invention, several are suitable: Paraplex G-62 available from C. P. Hall Company : Chicago, IL : Drapex 6.8 available from Witco Co.: Taft, LA (having on the average 4.2 epoxy groups per triglyceride); and Vikoflex 7170 from Elf Atochem. The current commercial use of epoxidized soybean oil is as plasticizer for polyvinyl chloride.

The use of acrylated epoxy oils in various resins has also been investigated. European Patent 81973 discloses the use of acrylated epoxidized triglycerides to synthesize photo-polymerizable coatings for glass. In the Japanese Patent 73-98883, acrylated epoxidized triglycerides is used to prepare ink vehicles that are capable of photocuring. In US Patent 4,025,477, and 3,931,075, acrylated epoxidized triglyceride is treated with

isocyanates and 2-hydroxyethylacrylate to give electron beam-curable coatings for metals with a Sward hardness of 14. In Japanese patent 75-126706, acrylated epoxidized triglyceride is used for photocurable ink vehicles used for textile printing. In Japanese Patent 73- 98885, acrylated epoxidized triglyceride is used with toluene di-isocyanate and 2- hydroxyethylacrylate to give a co-polymer that is capable of photocuring in textile printing applications. In French Patent 76-37 678, acrylated epoxidized triglyceride is used as a photocurable high flexibility coating for leather. In Japanese Patent 78-26116, acrylated epoxidized triglyceride is used as a photocurable ink vehicle that gives a faster cure and higher gloss. In Japanese Patent 77-137522, acrylated epoxidized triglyceride is used in conjunction with glycidyl acrylate-octylacrylate co-polymer and alumina filler to prepare a potting compound used for fluorescent light fixtures that eliminates transformer humming. In European Patent 90-203517, the use of acrylated epoxidized triglyceride as electron beam or UV curable thermosetting inks, coatings, and adhesives, is disclosed. W. Shi et al., in J. Photopolym. Sci. Technol., 5, 453, (1992), describe acrylated epoxidized triglyceride resin for high-gloss UV cured coatings. All of the above references are incorporated by reference in its entirety, for all purposes.

Investigation of the literature shows that the prior art allows acrylated epoxidized triglyceride resins to be used as surface coatings only. These are necessarily flexible, lightly cross-linked amorphous polymers, with little or no structural strength. These substances have been used in the prior art as varnishes, adhesives, protective coatings, ink vehicles, and high-gloss surface treatments, none of which requires any structural strength. As will be apparent below, in this disclosure, new chemical reactions and modifications allow epoxidized triglycerides to be polymerized to higher molecular weights and higher cross-link densities so that the new resins have structural strengths comparable to those of other liquid molding resins now in commercial use. Such use includes, but is not limited to, the high volume composite utilization fields of civil infrastructure, defense, aerospace, marine offshore, construction, bridge rehabilitation, automotive, farming equipment, electronics, etc.

Ring opening cure reactions of epoxy resins are well known. The use of diamines, anhydrides, dicarboxylic acids and diols have been reported in the literature. These

reactions are exceptionally easy when the epoxy ring that is undergoing the reaction is terminal, that is, at the end of the m lecule, which is the case in all commercially successful epoxy resins. In epoxidized triglycerides, however the epoxy group is necessarily internal, such that it is substituted on both sides by bulky alkyl groups, rendering it far less reactive towards the traditional ring opening polymerization reactants. Some of the resins described in this disclosure use the epoxy functional group of these triglycerides with various diols, diamines, anhydrides and diacids to produce highly cross-linked network polymers by ring-opening polymerization reactions.

The advantage of ring opening polymerization reactions is twofold: First, there is no by-product during the ring-opening polymerization, as all reactions are of the addition type; second, the degree of crosslinking, and therefore the final properties of the cured resin, can be controlled by merely adjusting the stoichiometry of the epoxy component and the second reactant, e.g., diols, anhydrides, diamines, dicarboxylic acids, alkoxides, etc.

Another advantage of such thermally induced epoxide ring-opening polymerization is, that unlike free radical addition reactions, ring-opening reactions can be stopped and re-started at will by decreasing or increasing the temperature, respectively. This allows individuals knowledgeable in the art to synthesize pre-polymers of desired molecular weight and viscosity, which can be kept at room temperature indefinitely (A-Stage), but which can be cured to a solid state in a mold merely by the application of heat (B-Stage).

Commercially successful epoxy resins usually consist of a two component system, the epoxy prepolymer and the curing agent, both as separate components. These components have to be metered, weighed, and mixed by the end user. The avoidance of two-component cure systems makes the resins described herein more attractive, as the end user need not be concerned with these complicated and error-prone mixing and metering steps.

Another advantage of the resins described in this invention is that the physical state and rigidity of the product can further be manipulated by the addition of various co-reactants having reduced or increased reactivity s that a desired fraction—or, in fact, all—of the epoxy groups are used in the final stage of the reaction. Such co-reactants include,

but are not limited to, primary and secondary alcohols and primary and secondary amines. The rate of the ring-opening polymerization can be adjusted by using desired amounts of ring-opening catalysts, which include, but are not limited to, cyanoguanidines, imidazoles, Lewis acid, metal alkoxides, and bases.

An added novelty of this disclosure is that the epoxy content of the epoxidized oils depends on the level of unsaturation of the oil used as raw materials. It is well known that oils from different plants such as, but not limited to, cotton, sunflower, corn, soy bean, and linseed have different amounts of unsaturation. Depending on the property desired in the final product, various oils, or mixtures thereof, may be used for the epoxidation reaction. Therefore, a raw material of the exactly desired epoxy equivalent can always be obtained by mixing epoxidized triglycerides from different plants. In this disclosure, the variation of unsaturation among the various plant oils is used to advantage. A promising development in this field is the future availability of triglycerides from genetically engineered plants which contain much higher levels of unsaturation and controlled distribution of fatty acid chain length than currently attainable from the natural plants.

The resins disclosed herein are more affordable than the hitherto commercially available liquid molding resins: their manufacture involves simple reactions that require simple reactors and machinery, and their origin from renewable resources makes them environmentally friendly and supportive of global sustainability.

Ring opening polymerization of epoxidized triglycerides has been disclosed in US Patent 3,291,764 where triethylenetetramine, p-phenylenediamine, phenylbiguanidine, etc., have been used as curing agents to give semi-fluid resins that were soluble in aqueous acid and used as a surface coating. Japanese Patent 73-102647 describes mixtures of epoxidized triglycerides, commercial epoxy resins such as Epikote 828 and diaminodiphenylmethane to give moldable solids; Frishinger, in Adv. Che. Ser. 239, 539, (1994) describes mixtures containing small amounts of plant triglycerides and mostly commercial epoxy resins and epoxy curing agents for the purposes of toughening commercial epoxy resins.

Roesch, et al., in Polymer Bull. (Berlin) 31,679, (1993) describes reaction of epoxidized triglycerides with maleic, succinic, hexahydrophtallic norbornanedicarboxylic

and phthalic anhydride. The reaction is run in a polypropylene melt with small amounts of epoxidized triglyceride dispersed in the melt where the dispersed phase is the epoxidized triglyceride and the continuous phase is polypropylene. The aim of this work is to produce toughened polypropylene.

Hydrogen peroxide oxidation of triglycerides to epoxidized triglyceride has been described by R. Oda, in Journal Society of Chemical Industry Japan, 41. 195-195 (1938) and by Y. Isii, in Journal Society of Chemical Industry, Japan, 43, 255-7, 315-7, 374-9 (1940)., and by Swern and Billen in Journal of Organic Chemistry, 67, 1786, (1945).

Maleinization of triglycerides have been the subject of many publications : Teeter. in J. Org. Chem. 22. 512, (1957) describes the reaction of maleic anhydride with conjugated fatty acids: Bickford, in J Am. Oil Chemist's Soc., 25, 254, (1948) describes maleinization of unconjugated triglycerides. Plimmer, in J. Oil Color Chemists' Assoc., 32, 99 (1949) describes the reaction of a number of different triglycerides with maleic anhydride. Maleic anhydride is known to react with triglycerides in an ene reaction, as well as insertion reactions giving oligomeric triglycerides. The procedures described in these papers are used to prepare maleic modified oils used in varnish manufacture. The reactivity of the anhydride has been used to react it with 2-hydroxyethylmethacrylate to give free radical curable resins for surface coating applications, as described in the Japanese Patent 81-64464, and for UV curable coatings, as described in the German Patent 89-3938149.

Glycerolysis of triglycerides has been known since antiquity. This is the traditional starting material for alkyd resins used as binders for "oil paints." There are many references to the formation of monoglyceride oils. There are also numerous references to polyesterification of monoglycerides with various diacids and dianhydrides. The co-monomers that have been used are phthalic anhydride, fumaric acid, pentaerythritol, glycerol, and aliphatic diacids, such as, but not limited to, succinic, glutaric, and suberic acid. The common point among the previous work is the formation of polyesters with saturated diacids and the use of the unsaturation contained in the fatty acid itself for "air drying", that is, peroxidative cross-linking of the products.

Monoglyceride polyesters have been described in the literature: For example, Japanese Patent 74-103144, describes phthalic anhydride alkyd for air drying paints; US

Patent 3,827,993 describes diethylene glycol-phthalic anhydride alkyd for surface coating; US Patent 4,740,367 describes fumaric acid alkyd used as an emollient base for skin and hair care products; Japanese Patent 73-125724 describes phthalic anhydride and pentaerythritol alkyd used for acid curable coatings; Japanese Patent 74-91317 describes phthalic anhydride and glycerol alkyd used for storage stable coatings; Japanese Patent 78-52321 describes phthalic anhydride and pentaerythritol alkyd used for air curable, water resistant coatings; Japanese Patent 80-62752 describes phthalic anhydride alkyd used for tough, air drying, glossy coatings; Japanese Patent 84-254873 describes isophthalic acid and polyethylene glycol alkyd for surface coatings.

Amidation of triglycerides has been discussed in a number of sources. Fatty acid amides are commercially important substances used as antistatic and softening agents for textiles. In British Patent 1248919, fatty acid amides made from fatty acids and diethanolamine to produce foamed resins are disclosed. There is no work in the literature on direct amidation of triglycerides, maleinization of the diethanolamide with maleic anhydride or on the polymerization of the maleate half-esters. The resin system disclosed here does not involve a polyester. It is only a half-ester of maleic anhydride—that is, a 1:2 adduct of the monoglyceride with maleic anhydride. This product is formed without any by-product by the reaction of the plant monoglyceride hydroxyl groups with maleic anhydride. The resulting molecule is unique and has not been synthesized before. The resin system disclosed herein does not depend on the air oxidation of the fatty acid unsaturation; in fact, those double bonds are intact in the product. The resin system described in this invention cures via the co-polymerization of reactive diluent and the maleate half-esters. In this invention, maleic anhydride is used as the esterification reagent and , among other reactions and processes, excess glycerol is used as a means of adjusting the cross-link density, thereby producing a structurally strong thermoset from natural triglycerides. The new thermoset and its modifications is recommended for use in composite manufacturing with high-modulus synthetic and natural fibers.

BRIEF DESCRIPTION OF THE INVENTION

The liquid resins described herein are derived from plant and animal oil triglycerides by suitably functionalizing the triglyceride with chemical groups that render it polymerizable. The triglyceride molecular structure is a combination of various triesters of fatty acids linked together with glycerol. The fatty acid residues are linear carboxylic acids containing from about 4 to about 30 carbon atoms, but preferably from about 14 to about 22 carbons and from about zero to about 4, or preferably from about 2 to 3 carbon-carbon double bonds. As obtained in nature, these double bonds are predominantly in the cis (Z) configuration and, in the case of polyunsaturated acids, not conjugated. The fatty acids derived from triglycerides include, but are not limited to the following: Lauric (C12:0), i.e., 12 carbon atoms long containing zero C=C double bonds, Myristic (C14:0), Palmitic (C16:0), Stearic (C18:0), Oleic (C18:1), Linoleic (C18:2), Linolenic (C18:3), Eicosanoic (C20:0), cis-11-Eicosanoic (C20:1), Docosanoic (C22:0) and cis-13-Docosanoic (C22:1). Typical plant oil triglycerides used for the purpose of this invention contain about 10-20 % saturated, about 20-30 % mono-unsaturated, about 40-60 % di-unsaturated, and about 5-15% tri-unsaturated fatty acid residues, but other distributions, both narrow and broad, of fatty acid residues can also be used for the thermoset and plastic resins described in this invention.

Typical fatty acid compositions of some plant oils are given in the following Table (extracted from Ashland Chemicals and Karlshamns Chart on Composition of Natural Fats and Oils).

Table-Compositi n of Natural Fats and Oils

Oil	C/C=C	Can-ola	Corn	Lin-seed	Olive	Palm	Pea-nut	Saffl ower	Soy	Lard	Fish
Lauric	12:0					0.1				0.3	
Myristic	14:0	0.1				1.2		0.1	0.1	1.7	1.3
Palmitic	16:0	4.1	11.5	5.5	16.9	**46.8**	11.0	6.7	10.5	26.2	13.6
Stearic	18:0	1.8	2.2	3.5	2.7	3.8	2.3	2.7	3.2	13.5	1.4
Oleic	18:1	**60.9**	26.6	19.1	**61.9**	37.6	**51.0**	12.9	22.3	**42.9**	**23.5**
Linoleic	18:2	21.0	**58.7**	15.3	14.8	10.0	30.9	**77.5**	**54.5**	9.0	0.8
Lino-lenic	18:3	8.8	0.8	**56.6**	0.6				8.3	0.3	
Eicosan oic	20:0		0.2		0.4	0.2	0.7	0.5	0.2	0.2	
cis-11-Eicosan oic	20:1				0.1	0.3		0.5	0.9	0.8	

This (incomplete) list shows the dominant triglyceride species (in bold) for typical oils and presents the relative level of C=C unsaturation of some oils used in this invention.

This invention prescribes the use of saturated and unsaturated triglycerides and their fatty acids residues from both plant and animal sources such as, but not limited to, lard, rape, palm, beef tallow, fish, soy, canola, sunflower, safflower, rice bran, corn, peanut, cottonseed and kolza. The C=C double bonds that constitute the unsaturation, create reactive sites that have traditionally been used for oxidative coupling reactions leading to

"air drying" of some plant oils. This is the chemistry of the well known alkyd resins used for paint and varnish binders. While there are many examples of the use of drying oils for surface coating applications, the unsaturation on the plant triglycerides is not sufficiently reactive to allow homo- or co-polymerizations of the molecule directly to give resins with any degree of structural strength or stiffness. US Patent 5,719,301 describes methods of increasing the level of conjugation in plant oils which have fatty acid residues with two or more unsaturated sites. The conjugated double bonds increase the reactivity of the unsaturated sites and these offer potential for additional reactivity such as in the air drying of Tung oil, or as a co-adhesive for particle board, cured at high temperatures for 24 hours, as described in US Patent 5,607,633. However, for those experienced in the art, the triglyceride molecule offers a number of reactive sites for functionalization. These include but are not limited to, the double bond, the allylic carbons, the ester group and the carbons alpha to the ester group. This invention discloses chemical reactions that use these active sites to introduce polymerizable groups on the triglyceride and the subsequent polymerization and composite formation using these new reactive triglycerides to give new polymers and composites with new composition of matter.

The triglycerides used in this invention were samples prepared from the crude plant oils by base extraction to remove free acids, and heated and filtered to remove the gummy non triglyceride residues. No attempt was made to deodorize, decolorize and to winterize the triglycerides. All of the resins described in this invention were characterized by the usual instrumental analysis techniques known by those knowledgeable in the art. These techniques include, but are not limited to, nuclear magnetic resonance spectroscopy, Fourier transform infra red spectroscopy, mass spectroscopy, ultraviolet spectroscopy, surface hardness test, differential scanning calorimetry, dynamic mechanical analysis and mechanical testing.

Description of Figures

Figure 1 shows a number of chemical pathways that are used for the purpose of introducing reactive sites on the triglyceride molecule which lead to the synthesis of the new monomers and composite resins disclosed in this invention.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 shows a number of chemical pathways that are used for the purpose of introducing reactive sites on the triglyceride molecule which lead to the synthesis of the new monomers and composite resins disclosed in this invention. The triglyceride can be directly oligomerized without any functionalization by oxidative coupling, sulfur vulcanization, olefin metathesis, photolysis, free radical co-polymerization with reactive diluents and polymerization with bis-maleimids to give viscous oils, soft rubbers and low glass transition temperature, Tg, solids. None of these materials are ultimately suitable as high modulus liquid molding resins.

The triglyceride, as shown in Figure 1, was suitably functionalized to the epoxidized triglyceride, to the hydroxylated triglyceride, and the hydroxy-formylated triglyceride by the reaction of the double bond functionality ; to the maleinized triglyceride by the reaction of the allylic carbon functionality and to monoglycerides and to hydroxy amids by the reaction of the ester functionality. All of these derivatives are new monomers that are capable of polymerization to rigid polymers suitable as liquid molding resins for high volume composite manufacturing applications, as discussed below.

EPOXIDIZED TRIGLYCERIDE

Conversion of the plant triglycerides to epoxidized triglycerides has been accomplished by reaction with hydrogen peroxide and the resulting epoxide can be polymerized in a number of ways. The epoxy groups were acrylated with acrylic acid and polymerized and crosslinked with free radical initiators in the presence of reactive diluents such as, but not limited to, styrene, divinyl benzene, methyl methacrylate, etc., to give rigid resins. Compounds such as, but not limited to, benzoyl peroxide, methyl ethyl ketone peroxide, hydrogen peroxide, and cumene hydroperoxide can be used as free radical

initiators. In the preferred embodiment. USP 245 (2.5-dimethyl 1-2.5 bis (2-ethylhexanoyl peroxyhexane) (peroxy ester) (by Witco Corp.) was used as the free radical initiator.

In addition to the free radically polymerizable acrylate ester, the acrylated triglyceride, now has newly formed hydroxyl and residual epoxy groups. In this invention, the residual epoxy groups are now used to chain extend the acrylated base resin with reactive difunctional molecules including, but not limited to, diamines, alkyl and aromatic diols, anhydrides, carboxylic acids, alkoxides, hydroxides and Lewis acids. When the base resin is thus modified, increased molecular weight and increased cross-link density of the resin allows the formation of cured resins with mechanical properties that are superior to unmodified acrylated epoxidized triglyceride resins produced according to prior art. Examples 1-9 describe the synthesis, curing and properties of resins prepared according to these reactions. Diamines that may be beneficially used include, but are not limited to, methylene dicyclohexyl amine, triethylene tetraamine, p-diaminobenzene, methylene dianiline, trimethyl hexamethylene diamine, diethanolamine, propanediamine, isophorone diamine. Diols that can be beneficially used include, but are not limited to, ethylene glycol. 2,5-hexanediol, 1,4-butanediol, pentaerythritol, bisphenol-A, 1,6-hexanediol, hydroquinone, sorbitol, inisitol, etc. Anhydrides that can be beneficially used include, but are not limited to, maleic anhydride, phthalic anhydride, pyromellitic dianhydride, nadic anhydride, succinic anhydride, cyclohexanedicarboxylic anhydride, etc. Alkoxides, hydroxides and Lewis acids that can be beneficially used include, but are not limited to, sodium and potassium hydroxide, methoxide, isopropoxide, aluminum trichloride, boron trifloride, etc.

In this invention, the newly formed hydroxy groups are also used for chain extension of the base resin by the use of appropriate hydroxy reactive difunctional molecules including, but not limited to, diisocyanates, ethylenicly unsaturated anhydrides, saturated anhydrides, diacids and diacid halides. These chain extending reagents include, but are not limited to, toluene diisocyanate, poly aromatic poly isocyanates, methylene diphenyl isocyanate, maleic anhydride, cyclohexane dicarboxylic acid anhydride, succinic acid, adipoyl chloride, etc. It is these very modifications that provide the increased

molecular weight and crosslink density to yield structurally strong resins and make the resins described in this invention unique.

The epoxidized triglyceride can be polymerized and crosslinked via ring opening polymerization by a large number of epoxy reactive molecules including, but not limited to, diamines, anhydrides, diols, dicarboxylic acids and they can be hydrolyzed in acidic medium to a polyol and can polymerize by ring opening polymerization by the use of suitable initiators. Diamines that may be beneficially used include, but are not limited to, methylene dicyclohexyl amine, triethylene tetraamine, p-diaminobenzene, methylene dianiline, trimethyl hexamethylene diamine, diethanolamine, propanediamine, isophorone diamine diaminodiphenyl sulfone, etc. Diols that can be beneficially used include, but are not limited to, ethylene glycol, 2,5-hexanediol, 1,4-butanediol, pentaerythritol, bisphenol-A, 1,6-hexanediol, hydroquinone, sorbitol, inisitol, etc. Anhydrides that can be beneficially used include, but are not limited to, maleic anhydride, phthalic anhydride, pyromellitic dianhydride, nadic anhydride, succinic anhydride, cyclohexanedicarboxylic anhydride, etc. Alkoxides, hydroxides and Lewis acids that can be beneficially used include, but are not limited to, sodium and potassium hydroxide, methoxide, isopropoxide, aluminum trichloride and boron trifloride. Acidic reagents that can be used include, but are not limited to, sulfuric, hydrochloric and hydrobromic acids., etc. As will be evident below, all of these resins are potentially useful liquid molding resins that cure without the use of reactive diluents or free radical initiators. The absence of any volatile and usually toxic reactive diluent makes these resins safer to handle than resins that are produced according to prior art. Another significant advantage of these resins over similar resins produced according to prior art, is that the cure reactions can be started and stopped at will. The cure reaction can be taken to any extent desired, the product can be kept for considerable periods and then cured to completion later. By those knowledgeable in the art, these resins can by conveniently formulated to A-Stage resins that are capable of curing to B-Stage in the mold. Hydrolyzed epoxidized triglycerides can also be used advantageously by polymerizing them with diisocyanates or reacting them with ethylenicly unsaturated anhydrides to free radically curable half-esters. Reagents that can be beneficially used include, but are not limited t , t luene diis cyanate, poly aromatic poly

isocyanates, methylene diphenyl isocyanate, and maleic anhydride. Examples 10-16 pertain to resins synthesized and cured by such reactions.

Epoxide curing reactions of epoxidized plant oils with bisphenol-A inevitably slow down as the reaction proceeds and epoxy concentration and accessibility decrease during polymerization. In this invention, the reduced reactivity of the epoxidized plant oil is offset by the addition of a reactive amine, such as, but not limited to, methylene dicyclohexylamine, triethylene tetra amine, p-diaminobenzene, diamino diphenylsulphone, isophorone diamine, diethanolamine, etc., in the B-Stage of resin preparation. The resulting product has essentially all of its epoxy groups used in polymerization and crosslinking reactions.

Epoxidized triglycerides can also be converted to resilient rubbers by careful control of molecular weight and cross link density. The resulting rubber can be used as a substitute for petroleum based rubber and can also be used as a rubber toughening agent in rigid composites.

HYDROXYLATED TRIGLYCERIDE

Plant triglycerides have been oxidatively hydrolyzed by hydrogen peroxide in the presence of formic acid. In this invention, the reaction medium is such that the initially formed epoxidized triglyceride cannot be isolated, but is converted directly to a mixture of dihydroxy and hydroxy-formate derivatives. The reaction is run in an aqueous solution of formic acid by emulsifying the triglyceride by high-shear stirring. Controlled addition of hydrogen peroxide at room temperature gives the poly-hydroxylated triglyceride. This mixture is then extracted with an organic solvent immiscible with water, such as, but not limited to, diethyl ether or chloroform. The organic phase is separated, dried and evaporated to yield the hydroxylated triglyceride. The removal of water can also be done without the use of an organic solvent by spray drying of the reaction product, using methods known by those knowledgeable in the art.

The product is a new triglyceride whose double bonds have been hydrolyzed to 1,2 diols and hydroxy formates. As such, the hydroxylated triglyceride can be

conveniently reacted with maleic anhydride to the maleate half-esters which are now capable of polymerizing free radically. Both the amount of hydroxylation and the amount of maleinization can be controlled to give new resins with the desired degree of unsaturation. By the optimization of these factors, liquid molding resins with high performance properties suitable for polymer composite applications can be produced. Due to the presence of additional carboxylic acid polar groups derived from maleic anhydride. and the unreacted hydroxyl groups, the adhesion of this resin to the fiber surface is stronger than the resins made according to prior art. Mixtures of hydroxylated triglycerides, and their acrylated or maleinated derivatives with other functionalized triglycerides can be used to obtain better fiber/matrix strength.

Hydroxylated triglyceride is also an excellent monomer that can be used with commercial epoxy resins as co-monomer and curing agent. This resin is composed of hydroxylated triglyceride, maleic anhydride, and a commercially available epoxy compound such as Epon 828 (Shell Chemical Co.), in a certain stoichiometric ratio having about 80-20% hydroxylated triglyceride, and about 20-80 % Epon resin. The preferred embodiment has the ratios of hydroxylated triglyceride:MA:Epon, between about 40:20:40 and about 50:20:30. This resin system can be cured thermally with tertiary amine catalyst. In this invention, the resin system contains no reactive and volatile diluents and does not require the addition of free radical initiators.

Analysis of the partially cured samples indicates that the hydroxylated triglyceride is first maleinated to the maleate half-ester and the carboxyl end of the molecule then reacts with the epoxy ends of the Epon resin. The ultimate tensile properties and toughness of this resin system can be optimized by the correct choice of stoichiometry, by those knowledgeable in the art. Examples 19-23 and 34-36 describe the synthesis, curing and properties of resins and composites made by these methods using a variety of plant oils and fibers.

MALEINIZED TRIGLYCERIDE:

The allylic positions on the triglyceride molecule are susceptible to many reactions, among which is the ene reaction with strong enophiles. The reactivity of the enophile

maleic anhydride with unsaturated triglycerides is well known and is the basis of "bodied" oils that have been traditionally used in naval stores and marine varnishes. Maleic anhydride is known to react with triglycerides in an ene reaction as well as insertion reactions giving oligomeric triglycerides. The reactivity of the anhydride has been used to react it with 2-hydroxyethylmethacrylate to give free radical curable resins for surface coating applications. The degree of maleinization of the triglyceride can be controlled by the amount of maleic anhydride used in the reaction and can be from about 1 to about 10, and preferably, about 1.5 to about 4 succinic anhydride residues per triglyceride. In the preferred embodiment, about 2 to 3, and preferably 2.6 succinic anhydride residues per triglyceride, was found to give optimal viscosity and reactivity properties. This invention describes new resins derived from maleinized triglyceride using the reactivity of the newly introduced succinic anhydride moiety with polyamines, polyols and bis epoxides. All of these resins have the previously mentioned property of not containing any volatile and reactive diluent and not requiring any free radical initiator to effect cure.

Maleinized triglyceride can be reacted with various diamines to give rigid resins, including, but not limited to, methylene dicyclohexyl amine, triethylenetetramine, jeffamine (polymeric diamine produced by Texaco), trimethylene hexanediamine, isophorone diamine, diethanolamione, urea, phenylene diamine, 1,6- hexanediamine, and tris(2-aminoethyl)amine. The resins have amido acid functional groups and should possess good adhesive properties with the commonly used reinforcing agents such as, but not limited to, glass, carbon, aramid and natural fibers. The reaction of the maleinized triglycerides with polyamines is exceptionally fast giving instantaneous cures at room temperature and leading to resins that are capable of curing under adverse environments such as cold climates.

Maleinized triglycerides can also be cured by alcoholysis of the anhydride. These reactions involve temperatures around 100 °C and require tertiary amine catalysts such as [2.2.2] diazobicyclooctane or dimethyl benzylamine and are slower reactions compared to amidolysis reactions. Diols and polyols that can be beneficially used to chain extend and cure maleinized triglycerides, include, but are not limited to bisphenol-A, ethylene glycol, glycerol, pentaerythritol, sorbitol, inisitol, glucose, sucrose, starch, polyvinyl alcohol, fatty acid monoglycerides, etc.

Epoxide ring opening polymerization with anhydride curing agents are well known and a large number of anhydrides such as, but not limited to, maleic anhydride, phthalic anhydride, pyromellitic dianhydride, nadic anhydride, succinic anhydride, cyclohexanedicarboxylic anhydride, etc., have been used to cure commercial epoxy resins. Imidazole or tertiary amine catalysts are usually employed to affect this reaction. In this invention, maleinized triglycerides have been used as curing agents and co-monomers for epoxy containing resins. Epoxy resins that can be beneficially used to manufacture polymers and composites, include, but are not limited to epoxidized triglycerides, commercial epoxy resins such as Epon 828 (Shell Chemical Co.), etc. Examples 24 and 25 describe the synthesis of resins made from maleinized triglycerides.

GLYCEROLYZED TRIGLYCERIDE

Alcoholysis of plant triglycerides with glycerol to yield monoglycerides is a well established reaction used in alkyd resin manufacture. In the prior art, monoglycerides are polyesterified with diacids or diacid anhydrides to short polyesters that are primarily used as paint binders for so called "Oil Paint". The short polyesters with pendant fatty acids are then allowed to "dry" by oxidative coupling reactions using appropriate catalysts known by those knowledgeable in the art as "drying agents". The air drying reactions are known to involve reaction of oxygen with the allylic position of the unsaturated fatty acid and necessarily require intimate contact of the resin with air. Hence, such polyesters can only be used in thin films as protective coatings and paint binders. While these resins give scratch resistance, anti-corrosive protection, and act as vehicles for pigments and fillers they possess no structural strength of their own.

Synthesis of monoglycerides from triglycerides involves ester interchange reactions and alcoholysis of 2/3 of the ester groups of the triglycerides. In the process, the positional isomers of the various fatty acids are randomized, giving mixtures that are mostly monoglycerides but also contain diglycerides, unreacted triglycerides and unreacted glycerol. Mono-and di-glycerides also exist as positional isomers. Those knowledgeable in the art are aware of various catalysts and reaction conditions required for the preparation of monoglycerides with controlled amounts of di and negligible amount of triglycerides.

The synthetic route to the new monomers described in this disclosure starts with the glycerolysis of fatty acid triglycerides to give monoglycerides. The monoglyceride product is actually a mixture containing mostly mono but also, in smaller amounts, di- and triglycerides. Mono- and diglycerides are positional isomers, and the mixture also contains some unreacted glycerol whose amount can be adjusted by adjusting the feed ratio. The complex monoglyceride mixture is then reacted with maleic anhydride under conditions that lead to the formation of the maleate half-esters of mono- and diglycerides and of the excess glycerol. Therefore, all the species in the final product have now been rendered polymerizable by the introduction of the reactive maleate unsaturation. This monomer mixture has not been synthesized before and constitutes a new composition of matter. The resin can then be diluted with reactive monomers such as styrene and is ready for use. In this invention, the synthesis of the monoglycerides was carried out in such a way that the final mixture contained about 80-90 % monoglycerides, about 4-10% diglycerides and about 2-6% unreacted glycerol. All of the components were therefore mono, di or trihydroxy compounds. The maleinization reaction was carried out in the presence of a base catalyst such as, but not limited to, calcium hydroxide and under mild thermal conditions, e.g., between about 50 to about 100 C, and preferably about 80 C, such that only maleate half-esters were formed and no attempt was made to increase the molecular weight by polycondensation reactions. The product of the reaction is predominantly monoglyceride-bis maleate half-ester, in a mixture with diglyceride monomaleate halfester and glycerol trimaleate half-ester. The judicious choice of stoichiometry and conditions of the glycerolysis step determined the relative ratios of mono, di and triols in the maleinization mixture and this in turn, determined the relative ratios of mono, di and trimaleates in the maleinized mixture. For those knowledgeable in the art, the significance of the ratio of mono, di and tri unsaturated monomers in a polymerization mixture is clear. The desired cross-link density and cross-link segment lengths can be obtained by adjusting the relative amounts of the above unsaturated products.

Maleinized monoglyceride mixture was then mixed with reactive diluents such as, but not limited to, styrene, α-methyl styrene, methyl methacrylate, divinyl benzene, ethylene glyc l dimethacrylate, etc. and cured with the previously mentioned free radical

initiators to give rigid thermoset resins. The resin formulation can be further improved by the use of oligomeric cross-linking agents, by adjusting the amount of unreacted glycerol, and by air drying of the unsaturation present in the fatty acid residue. The presence of unreacted glycerol (a monomer with a functionality of 3), which itself is maleated in the next step, constitutes a very novel and convenient method for adjusting cross-link density, whereby the physical properties of the final thermoset can be optimized. The presence of the carboxylic acid group on the maleate half-esters was observed to provide good adhesion with the commonly used reinforcing agents such as, but not limited to, glass, carbon and aramid fibers as well as a number of naturally occurring fibers. These improvements produce a resin system that can be used alone, or reinforced with high-modulus fibers such as, but not limited to, glass, carbon, Kevlar® (Aramid Fiber, DuPont Co.) and natural fibers such as, but not limited to, sisal, jute, hay, hemp, and cotton.

The use of natural fibers with the resins described herein promises to give economical, potentially biodegradable, engineering materials with a high level of vegetable-based raw materials. Such materials have a low market cost, they are attractive with respect to global sustainability and should find commercial use as the composite industry becomes more environmentally responsible in the near future. The resins described can be modified by various additives to improve adhesion to these fibers, thereby significantly improving their physical properties and hydrolytic stability. Some of these resins can be used as sizing agents for the natural fibers by controlling the type of functional groups, e.g., by using hydrophilic hydroxylated oils, which contain sufficient vinyl reactive sites, e.g. by maleinization, to bond to the matrix, which by choice can be more hydrophobic than the sizing agent. Typically, the sizing agent concentration would be of the order of 1% by wt compared to the matrix. The resulting sizing would provide a strong bond between the fibers and the matrix, which is essential to the manufacture of high performance composite materials. The composites thus formed have physical properties that compare favorably with the previously mentioned petroleum-based commercially successful resins.

To further increase the functionality of the monoglycerides, the unsaturation when present on the monoglyceride, can be hydroxylated in the same manner described in the

previous section. Hydroxylation of the monoglyceride mixture was done prior to maleinization under the same reaction conditions as used wh n hydroxylating the triglyceride. This provided additional hydroxyl groups along the fatty acid chain, thus increasing the overall functionality of the molecule and its ability to form highly cross linked rigid composites. Maleinization of the resulting hydroxylated monoglyceride was then done again using a base catalyst such as, but not limited to, dimethyl benzyl amine, calcium hydroxide, etc.. The maleinized hydroxylated monoglyceride is now suitable for mixing with a reactive diluent, such as, but not limited to, styrene, a-methyl styrene, methyl methacrylate, divinyl benzene, etc., and curing via free radical polymerization.

A major advantage of the resin system described here is that the polymerization reaction takes place on the double bond provided by the maleate half-ester. This invention does not use the unsaturation of the fatty acid residue for polymerization reactions, except in the previous case using maleinized hydroxylated monoglyceride, where the initial unsaturation was first hydroxylated prior to maleinization. Therefore, the final properties of the resin that are dependent on crosslinking reactions, are quite insensitive to the source of triglycerides used as raw materials. This allows the use of any triglyceride of plant or animal origin or their mixtures as raw material. The molecular weight and cross-link density would not be effected by seasonal or geographical changes in the raw material. This makes available a large number of saturated and unsaturated triglyceride sources such as, but not limited to, lard, rape, palm, beef tallow, fish, soy, canola, sunflower, safflower, rice bran, corn, peanut, cottonseed and kolza, some of which are essentially inedible and of no other use industrially, as raw materials for the resins disclosed herein.

The glycerolized triglyceride molecules, as a polyol mixture, was also reacted with various diisocyanates such as, but not limited to, toluenediisocyanate, isophorone diisocyanate, methylene diphenyldiisocyanate and polyaromatic polyisocyanate in the presence of tertiary amine catalysts to give foamable rigid thermoset resins. Examples 26-28 describe the synthesis of resins using this chemical approach.

AMIDATED TRIGLYCERIDE

Transamidation of esters with primary amines is a well known reaction and triglycerides have been amidated with various amines to yield industrially important compounds. Such fatty acid amides have found use as textile softening agents, anti static agents and sizing agents.

In this invention, transamidation of triglycerides with diethanolamine and tris(2-aminoethyl)amine gave successful rigid resins, suitable for composites. In the case of diethanolamine, the choice of reaction conditions was such that transamidation took place without any transesterification. The resulting mixture was found to contain fatty acid monoamide as positional isomers and glycerol, all polyhydroxy compounds. As such, these polyols were polymerized with various diisocyanates such as, but not limited to, toluene diisocyanate, isophorone diisocyanate, methylene diphenyldiisocyanate and polyaromatic polyisocyanate in the presence of tertiary amine catalysts to give foamable rigid thermoset resins.

The triglyceride diethanolamine amide mixture was then reacted with maleic anhydride without further separation to give a mixture of bis-maleate and tris-maleate half-esters. The maleinization reaction was run under mild conditions and no attempt was made to polyesterify the mixture. This mixture was then combined with reactive diluents and polymerized with free radical initiators to yield a rigid thermoset resin.

The rigid thermoset resin was found to be biodegradable and exhibited substantial weight loss due to the action of fungi and bacteria under aerobic conditions when exposed to a moist soil environment at room temperature for several weeks. Biodegradation tests were done at a burial depth of about 2 inches in loam soil containing 30% by wt of water. The biodegradability of this oil-based resin has the potential for many new applications where the biodegradability of the composite is either an important part of its in-service performance, or facilitates its disposal in terrestrial or aquatic environments.

The reaction of triglycerides with tris(2-aminoethyl)amine was run under such conditions that the only products were diaminoamide of the fatty acids and glycerol. This product was found to be an excellent co-monomer for curing epoxy resins and excellent

thermoset resins were obtained when Epon 828 commercial resin or epoxidized triglycerides were used as the epoxy component. Examples 29-31 describe the synthesis of resins according to this chemical approach

EXAMPLES

While there is shown and described certain specific structures embodying the invention, it will be manifest to those skilled in the art that various modifications and rearrangements of the parts may be made without departing from the spirit and scope of the underlying inventive concept and that the same is not limited to the particular forms herein shown and described. The examples illustrate representative products and are given by way of illustration only and are not to be considered as being limiting.

Example 1

100 g of epoxidized triglyceride (G-62 Paraplex from C. P. Hall Co.) having an average of 4.2 epoxy groups per triglyceride and an iodine number of 5, and 23 g of acrylic acid were mixed, after which 0.2 g of hydroquinone and 10 drops of 30 % benzyltrimethyl ammonium hydroxide solution in methanol were added. The mixture was heated and stirred at 110°C for 12 hours or until spectroscopic examination showed the disappearance of the desired amount of the epoxide groups. This is the acrylated base resin. The acrylated base resin was mixed with styrene and divinyl benzene in the ratio 100:45:5 and had a viscosity of 70-80 cps. as measured by a Brookfield viscometer. This mixture when cured with USP-245 free radical initiator at 90 °C for one hour and 110 °C for one hour, produced a rigid resin with flexural modulus of 723 MPa and surface hardness of 79 (Shore D). The corresponding values for commercial amine cured epoxy resins are 2000 MPa and 85(Shore D)

Example 2

80 g of the acrylated base resin, having approximately 8% of the epoxy groups unreacted, was mixed with 10 g of maleic anhydride and heated to 80 °C for 4 hours. An

increase in viscosity was observed along with the disappearance of the remaining epoxy group absorbance in the IR spectrum. This is the unsaturated anhydride modified base resin. When this resin was cured using the method of Example 1, a 60% improvement in the flexural modulus and 5% improvement in surface hardness was observed. The glass transition temperature, Tg, of the cured resin was found to be 135 °C .

Example 3

80 g of the acrylated base resin, having approximately 8% of the epoxy groups unreacted, was mixed with 2.5 g of maleic acid at 110 °C and stirred for 2 hours. An increase in viscosity was observed. This is the maleic or fumaric acid modified base resin. This resin when cured according to the conditions described in Example 1 gave flexural modulus of about 2 GPa, surface hardness of 80 (Shore D) and a Tg of 102 °C. The flexural modulus of commercial polyester resins is about 3.0 GPa.

Example 4

400 g of acrylated base resin was mixed with 44 g maleic acid and heated at 95 °C for 4 hours. An increase in viscosity was observed. Upon mixing the maleinated triglyceride with styrene and divinyl benzene in the ratio 100:45:5, respectively, the resulting resin had a viscosity of 2000 cps. which upon curing with 1.5% USP 245 at 65 °C for 1 hour with a postcure at 110 °C for 1 hour. produced a rigid thermoset with a tensile modulus of 2.5 GPa.

Example 5

80 g of the acrylated base resin, having approximately 8% of the epoxy groups unreacted, was mixed with 4 g of polyaromatic polyisocyanate (PAPI manufactured by Dow Chemical, Midland Mi.), and 0.1 g of diazobicyclo [2.2.2]octane was added as a catalyst. The mixture was heated at 60°C for 2 hours. An increase in viscosity and the disappearance of the isocyanate absorption in the IR spectrum was observed. This is the diisocyanate modified base resin. This resin when cured according to the conditions described in Example 1, gave a flexural modulus of about 1.2 GPa , Tg of 77 C and a

surface hardness of 78 (Shore D). The flexural modulus of commercial vinyl ester resins is about 2 GPa.

Example 6

80 g of the acrylated base resin, having approximately 8% of the epoxy groups unreacted, was heated at 110°C under 1 mm Hg pressure with a downward distilling apparatus to remove unreacted acrylic acid. Approximately 4 ml of acrylic acid was removed. This base resin was mixed with 2 g of methylene dicyclohexyl amine and then diluted with reactive diluent styrene to the extent of 100 g of resin to 45 g of styrene. This mixture was degassed by purging with nitrogen for 5 minutes and 1.5 % USP 245 radical initiator. Cure of this mixture at 110°C for one hour and postcure at 130°C for 3 hours gave the cross-linked diamine modified base resin.

Example 7

80 g of the acrylated base resin, having approximately 8% of the epoxy groups unreacted, was treated as previously described so that no unreacted acid was left in the mixture. This base resin was treated with 0.2 g of titanium isopropoxide and heated at 80°C for 2 hours. Color change to a deep red, and an increase in viscosity was observed. This is the ring opening modified base resin. This resin, when cured according to the conditions described in Example 1, gave flexural modulus of about 1 GPa, surface hardness of 78 (Shore D) and a Tg of 68 °C.

Example 8

80 g of the acrylated base resin, having approximately 8% of the epoxy groups unreacted, was mixed with 9 g of cyclohexane dicarboxylic anhydride and heated for 1 hour at 110°C. An increase in viscosity and reduction in the epoxide absorption in the IR spectrum was observed. This is the saturated anhydride modified base resin. This resin when cured according to the conditions described in Example 9 gave dynamically measured storage modulus of about 2 GPa and a Tg of about 75 °C. Dynamic mechanical tests were conducted at a frequency of 1 cycle/sec and a heating rate of 5 °C/min, using a Rheometrics dynamic mechanical analyzer

Example 9

100 g of the acrylated base resin, or any of the modified resins, was mixed with 45 g of styrene and 5 g of divinyl benzene. The mixture was degassed by purging with nitrogen for 5 minutes. 1.0 g of USP 245 free radical initiator was added, and the mixture was injected into a resin transfer mold (RTM) containing a preform made of woven glass fiber with a suitable sizing. The mold was heated at 110°C for 40 minutes and then at 130°C for 2 hours to give a glass-fiber-reinforced composite. Neat-resin properties of resins cured according to this example were measured and the flexural modulus E (MPa), glass transition temperature, Tg (°C) and dynamically measured storage modulus E' (GPa) of the base resin was found to be E = 400 MPa, Tg = 67 °C and E' = 0.77 GPa. For the maleic anhydride modified resin, E = 960 MPa, Tg = 102 °C and E' = 1.60 GPa.

The composite properties of the base resin with 45 % woven glass fiber were as follows, maximum tensile strength, 38.9 ksi (268 MPa) (according to ASTM D 3039-76); tensile modulus 2.49 Msi (17.2 GPa) (according to ASTM D 3039-76); flexural strength 260 MPa (37.3 ksi, according to ASTM D-790-86); and flexural modulus 11.3 GPa (1.64 Msi, according to ASTM D 790-86).

The fracture toughness K_{Ic}, of the woven glass fiber reinforced base resin measured by center notch tension (ASTM Number pending) was determined to be about 32 MPa. $m^{1/2}$, using fracture mechanics specimens with typical dimensions of width w = 3.6 cm, center crack length 2a = 2.0 cm, and thickness B = 0.33 cm. In these fracture experiments, the typical maximum applied fracture loads were about 350 N (3,755 lb).

Composites manufactured with commercially successful orthophthalic acid - propylene glycol type polyesters cured similarly and having similar glass fiber contents have tensile strengths about 500 MPa and tensile modulus of about 20 GPa

Example 10

100 g of epoxidized triglyceride was mixed with 45 g of methylene dicyclohexyl amine and 1.0 g of 2-methyl imidazole. The mixture was heated at 90 °C for 1 hour and

then transferred to an RTM mold containing glass fiber preform. The mold was heated at 130 °C for one hour to give a rigid thermoset.

Example 11

40 g of epoxidized triglyceride was mixed with 16 g of isophthalic acid and 0.3 g of 2-methylimidazole and the mixture was heated at 90 °C for 1 hour. The mixture was then transferred to a mold and heated for an hour at 140 °C to give a rigid thermoset resin.

Example 12

40 g of epoxidized triglyceride was mixed with 18 g of phthalic anhydride and the mixture was stirred and heated at 90 °C until phthalic anhydride dissolved. The resulting mixture was transferred to a mold and heated for 1 1/2 hours at 140 °C to give a rigid thermoset resin.

Example 13

100 g of epoxidized triglyceride was mixed with 30 g of bisphenol-A and 0.6 g of 2-methylimidazole. The mixture was stirred at 100 °C for one hour or until it reached the desired viscosity and then transferred to a mold. The mold was heated at 180 °C for 1 hour to give a rigid thermoset resin.

Example 14

122 g of epoxidized soyoil was mixed with 46 g bisphenol-A and heated at 90 °C for 20 hours. To the resulting viscous oil, 0.2 g of methylimidazole and 17 g of diaminodiphenylsulphone was added. The mixture was poured into a mold and cured at 180 °C for 1 hour and postcured for 6 hours to yield a red colored transparent rigid solid. The reaction could be stopped and restarted at any stage simply by changing the temperature. IR Spectral analysis of the product indicated that 88% of all epoxy groups had been consumed. The resulting solid had a Tg at 54 °C. The physical properties of this resin are approximately half that of commercial terephtallic based liquid molding polyester

resin. Solvent extraction with acetone revealed 1.5% unreacted monomer. The final volume had an equilibrium volumetric swelling ratio of 2.2 in toluene.

Example 15

40 g of epoxidized triglyceride was mixed with 0.8 g of borontrifloride-ethylamine complex and transferred to a mold. Heating at 90 °C for one hour gave a rigid thermoset resin.

Example 16

40 g of epoxidized triglyceride was mixed with 1.0 g of titanium isopropoxide and heated at 60 °C for two hours. The product was a rigid thermoset resin. The reaction could be stopped at any time by adding 1 ml of water and resilient rubbers of different toughness could be obtained according to the extent of reaction.

Example 17

40 g of epoxidized triglyceride was emulsified with 20 g of water and 4 g of concentrated hydrochloric acid by high shear stirring at room temperature. The mixture was taken to 40 °C and stirred for one hour. The mixture was allowed to phase separate and the top layer of hydrolyzed epoxidized triglyceride was removed and dried by heating under 4 mm pressure at 70 °C for 2 hours to give 32 g of the hydrolyzed epoxidized triglyceride. 20 g of the hydrolyzed epoxidized triglyceride was mixed with 12 g of polyaromatic polyisocyanate (PAPI) and 0.3 g of [2.2.2]diazobicyclooctane. The mixture became viscous at room temperature in 30 minutes and was transferred into a mold and heated at 60 °C for 2 hours to produce a rigid thermoset resin.

Example 18

27 g of maleic anhydride was added to 32 g of the hydrolyzed epoxidized triglyceride of Example 16, and the mixture was heated to give a viscous oil. The oil was diluted with 22 g of styrene and 1.0 g of USP 245 free radical initiator was added. Heating the mixture at 80 °C for 1 hour and at 110 °C for an additional hour gave a rigid thermoset

resin. The flexural modulus and Tg of the cured resin were 1020 MPa and 70 °C. respectively. The physical properties of this resin are generally comparable to those of commercially available orthophthalic polyesters.

Example 19

1000 g of plant triglyceride was mixed with 1000 ml of 88% formic acid in a reactor equipped with a cooling jacket. 500 ml of 30% hydrogen peroxide was added in 50 ml portions in 10-minute intervals. The reaction was vigorously stirred for 5 hr. The emulsion was poured into a separator funnel and extracted with ether. The water layer was discarded, and the ether layer was washed with water, dilute sodium bicarbonate solution, and saturated sodium chloride solution, respectively. The resulting ether solution was dried over magnesium sulfate, and the ether was removed by a rotary evaporator to yield 1150 g of hydroxylated soyoil.

Example 20

144.4 g of maleic anhydride (MA) and 0.4 g of hydroquinone were added to 400 g of hydroxylated triglyceride in a 1 L round-bottom flask. The mixture was warmed to 50 °C under stirring to dissolve all the maleic anhydride. The temperature was further raised to 100 ^{0}C, and 15 ml of benzyl dimethyl amine was added in two portions. The reaction was kept at 100 ^{0}C for 3 hr. under stirring to obtain the maleinized product with a 4:1 molar ratio of MA to hydroxylated triglyceride.

Example 21

100 g of maleinized hydroxylated triglyceride from Example 20 was mixed with 45 g of styrene and 5 g of divinyl benzene ; 2.25 g of USP 245 was added, and the mixture was degassed by purging with nitrogen for 10 minutes. The mixture was injected into an RTM mold containing 76 wt% glass fiber preform consisting of two mats TPI QM6408 fabric. The mold was then heated at 65 ^{0}C for 1.5 hr and 120 ^{0}C for 1 hr to provide a

cured fiber-reinforced composite sample. The composite properties were measured and are shown with those of a commercial composite vinyl ester resin in the following Table:

Table-Properties for Hydroxylayed Maleinized Soyoil and Commercial Composites

Property	Dow DK 411C50 Fiber Glass Composite	Hydroxylated Soy Oil Fiber Glass Composite
Glass Fiber Content wt%	76	76
Tan Delta Peak °C	128	128
Flex Modulus MSI	5.2	5.0
Flex Strenth at Break KSI	118	97
Compresion Strength KSI	42	29
Short Beam Shear Strength KSI	7.6	5.5

Example 22

10 g of hydroxylated triglyceride was mixed with 10 g of Epon 828 and 5 g of maleic anhydride. The mixture was warmed up to 60 ^{0}C to dissolve the maleic anhydride and 2 ml of benzyldimethylamine was added. The resin was poured into a mold with or without fiber preform and cured at 90 ^{0}C for 1 hour to yield a rigid thermoset sample.

Example 23

Maleinization of triglyceride was accomplished by following procedures described in the literature, by heating 100 g of triglyceride with 27 g of maleic anhydride at 200 °C

for 2 hours. The sample contained 0.002 moles of anhydride per gram. 100 g of the maleinized triglyceride was cooled to 4 °C and mixed with 30 g of methylene dicyclohexylamine, also cooled to 4 °C, and the mixture was stirred and allowed to come to room temperature. The mixture was then heated at 80 °C for one hour to give a rigid thermoset resin.

Example 24

100 g of maleinized triglyceride from Example 23 was mixed with 18 g of pentaerythritol and heated at 130 °C to give a rigid thermoset resin.

Example 25

50 g of maleinized triglyceride from Example 23 was mixed with 40 g of Epon 828 commercial epoxy resin and 0.2 g of 2-methylimidazole. The mixture was placed in a mold and heated at 80 °C for one hour to give a rigid thermoset resin.

Example 26

Glycerolysis of triglycerides were done by following the procedures given in the literature. Thus, 240 g of triglyceride was mixed with 60 g of glycerol and 0.2 g of calcium hydroxide and heated at 230 °C for 4 hours. The resulting mixture contained 88% monoglyceride, 4 % diglyceride and 4% triglyceride and 4% glycerol. This is the glycerolized triglyceride mixture. To 40 g of the glycerolized triglyceride mixture, 20 g of maleic anhydride was added and the mixture heated at 100 °C for 2 hours to give maleinized monoglyceride. The resulting mixture was diluted with 25 g styrene and 1 g divinylbenzene and 1 g of USP 245 free radical initiator was added. The mixture was cured in a mold at 70 °C to give a rigid thermoset resin. The flexural modulus and Tg of the cured resin were 720 MPa and 135 °C, respectively. The commercially successful polyester resins have heat deflection temperatures of about 80 °C.

Example 27

30 g of glycerolized triglyceride mixture from Example 26 was mixed with 15 g of

isophorone diisocyanate and 0.1 g [2.2.2]diazobicyclooctane. Curing the mixture at 60 °C for 3 hours gave rigid thermoset resins, while curing at 60 °C for 1/2 hour gave a foamed thermoset resin with a specific gravity of 0.2.

Example 28

1 g of hydroxylated monoglyceride was heated to 60 °C. 0.25 g of hydroquinone radical inhibitor, 0.5 g of maleic anhydride, and 6 drops of dimethyl benzyl amine were added and the reaction heated at 90 °C for one hour forming the maleinized hydroxylated monoglyceride. The maleinized hydroxylated monoglyceride was heated to 90 °C, mixed with 1 g styrene, and allowed to cool to room temperature. 2 drops of USP 245 free radical initiator were added and the mixture cured at 90 °C for one hour giving a rigid thermoset polymer.

Example 29

32 g of triglyceride was mixed with 10 g diethanolamine and heated to 180 °C. The mixture slowly became one phase and was heated for a total of 2 hours, or until the mixture was soluble in methanol. This is the triglyceride diethanolamine amide. To this mixture 16 g of maleic anhydride was added and the mixture was kept at 100 °C for 15 minutes to give the maleinized fatty acid amide. This mixture was mixed with 22 g styrene and 1 g USP 245 free radical initiator and heated in a mold to give a rigid thermoset resin. The flexural modulus of the cured resin was 340 MPa .

Example 30

18 g of toluenediisocyanate was added to 40 g of the triglyceride diethanolamine amide obtained in Example 27. The reaction started at room temperature and the mixture gelled in 30 minutes. Continued heating at 125 °C for one hour gave a rigid thermoset resin.

Example 31

40 g of triglyceride was mixed with 18 g of tris(2-aminoethyl)amine and the mixture was heated at 160 °C for one hour. The resulting product was mixed with 90 g of Epon 828 and polymerized by heating at 70 °C for 3 hours. The result was a rigid thermoset resin.

Example 32

333 g of acrylated epoxidized triglyceride was mixed with 150 g styrene, 17 g divinyl benzene, and 10 g USP 245 free radical initiator. The mixture was degassed by purging with nitrogen for 5 minutes. The resin mixture was then injected at 30 psi into an RTM mold containing a preform made from two non-woven hemp fiber mats at 0/90 fiber orientation. The fiber volume fraction of the resulting composite was 20% hemp by weight. The mold was heated at 90 °C for 1 hour and at 110 °C for one hour to produce a rigid hemp fiber composite.

Table-Hemp Composite Properties

Tensile Strength	Tensile Modulus	**Toughness, K_{1c}	**Fracture Energy	Density
35 MPa	4.4 GPa	3 MPa.$m^{1/2}$	2 KJ/m^2	1.104 g/cm^3

**Determined using Center-Notched specimens

Example 33

200 g of acrylated epoxidized triglyceride was mixed with 90 g styrene, 10 g divinyl benzene and 6 g USP 245 free radical initiator. The mixture was degassed by purging with nitrogen for 5 minutes. Separately 60 g of straw fibers were pressed into a preform in a molding press and transferred to an RTM mold. The resin mixture was injected and the mold was heated at 90 °C for 1 hour and 110 °C for 1 hour to produce a

rigid straw fiber reinforced composite.

Example 34

100 g of maleinized hydroxylated triglyceride was mixed with 45 g styrene, 5 g divinyl benzene and 1.5 g USP 245 free radical initiator. The mixture was degassed by purging with nitrogen for 5 minutes. The resin mixture was injected into an RTM mold containing woven carbon fiber preform and the mold was heated at 90 °C for 1 hour and 110 °C for 1 hour to produce a rigid carbon fiber reinforced composite.

Example 35

A series of maleinized hydroxylated triglycerides (prepared via Example 20) derived respectively, from Olive Oil, Safflower Oil, Soybean oil and mixtures of Soybean-Olive oil, were prepared (Example 21), using 100 g of maleinized hydroxylated oil with 45 g styrene, 5 g divinyl benzene and 1.5 g USP 245 free radical initiator.

Table-Properties of Maleinized Hydroxylated Plant Oils

Plant Oil	No C=C Bonds/Triglyceride	Tg °C	Hardness Shore D	Storage Modulus GPa Room Temp	Crosslink Density at 140 °C mol/m3	Functional Groups in Oil
Olive Oil	2.8	81	74.6	1.04	3952	1.23
Soy/Olive	3.7	91	77.4	1.31	4397	1.41
Soy Oil	4.6	102	82.6	1.64	4812	1.65
Safflower	5.1	117	84.3	1.90	5525	1.81

The mixture was degassed by purging with nitrogen for 5 minutes. The resin mixtures

were cured at 90 °C for 1 hour and 110 °C for 1 hour to produce rigid thermosets. The properties were evaluated as a function of the plant oil used and are shown in the above Table. As the level of C=C unsaturation increases, the amount of functionalized triglycerides also increases resulting in a more highly crosslinked thermoset. As the degree of crosslinking increases, the Tg, Hardness and Modulus increase proportionately. The number of functionalized groups per triglyceride, following the addition of maleic annhydride, was determined by nuclear magnetic resonance (J. La Scala and R. P. Wool; paper to be published). With the above information, high performance resins can be designed with respect to triglyceride structure to give hard, or soft thermosets with optimal properties.

Example 36

330 g of maleinated hydroxylated triglyceride was mixed with 12 g Dow Derakane 411 vinyl ester resin and 6 g of USP 245 free radical initiator. The mixture was degassed by purging with nitrogen for 5 minutes. The resin mixture was injected into an RTM mold containing woven glass fiber preform and the mold was heated at 90 °C for 1 hour and 110 °C for 1 hour to produce a rigid glass fiber reinforced composite.

Example 37

8 g of acrylated epoxidized triglyceride was mixed with a range of 2- 8 g of Dow Derakane 411 vinyl ester resin. and 0.2 g of USP 245 free radical initiator. The mixture was purged with nitrogen for 5 minutes and heated at 90 °C for one hour, and at 110 °C for one hour, to give a rigid thermoset resin. Commercial bisphenol-A vinyl ester resins have the following cured neat resin properties: tensile modulus, about 3 GPa; Elongation at break, 10%; flexural modulus, 2.8 GPa; and heat deflection temperature, 75 C. The properties of resins prepared according to Example 37 are similar in terms of cure characteristics, processing and their optical, thermal and mechanical properties.

Example 38

80 g of maleinized fatty acid monoglyceride was mixed with 30 g of styrene and 20 g of glass fibers chopped to 6 mm length. The mixture was tumbled in a ball mixer for 10 minutes to give a bulk molding compound (BMC) resin with 15% glass content. The resulting mixture was mixed with 0.6 g 10% cobalt naphtenate and 1 g methyl ethyl ketone peroxide and was placed in a mold containing chopped glass fiber. The molding compound was allowed to cure at room temperature to give a rigid chopped fiber reinforced composite. The resulting composite product had surface properties and mechanical properties that were similar to BMC compounds using commercially available polyester resins

Example 39

100 g of epoxidized triglyceride was mixed with 30 g of bisphenol-A and 0.6 g of 2-methylimidazole. The mixture was stirred at 100 °C for one hour, or until it reached the desired viscosity and then transferred at atmospheric pressure into an open mold which was preheated to 90 °C and which contained 18g of 0/90 glass fiber woven cloth. The mold was heated at 180 °C for 1 hour to give a rigid thermoset glass fiber reinforced composite.

Example 40

100 g of maleinized fatty acid diethanolamide was mixed with 30 g of styrene, 1.5 g of cobalt naphtenate and 1.0 g of methyl ethyl ketone peroxide. The mixture was hand laid up on a 50 cm X 50 cm sample of 600 g/ m^2 chopped glass fiber mat and allowed to cure at room temperature. The product was a rigid glass fiber reinforced composite.

Example 41

40 g of maleinized fatty acid monoglyceride and 40 g of maleinized fatty acid diethanolamide was mixed with 30 g of styrene, 0.6 g dimethyl aniline and 0.8 g benzoyl peroxide. The mixture was degassed for 5 minutes by purging with nitrogen and heated in a mold at 90 °C for 1 hour and at 110 °C for 1 hour. The product was a rigid thermoset resin.

Example 42

1500 g of acrylated epoxidized triglyceride was mixed with 750g styrene, 113 g divinyl benzene, 18g cobalt naphthalate and 68g Trigonox 239 free radical initiator. The resin was infused into a glass fiber (50% V_f) preform (QM6408 E-Glass, 2 plies) by Seemann's Composite Resin Injection Molding Process (SCRIMP). The composite was cured for 12 hours at room temperature and postcured for 2 hours at 150 °C, resulting in a rigid thermoset composite. The glass transition temperature was determined to be 80 °C.

Comparison of Plant Oil and Commercial Vinyl Ester Fiber Glass Reinforced Composites

Materials	Testing Direction	Tensile Strength KSI ASTM D3039-76	Youngs's Modulus MSI ASTM D 3039-76	Compressive Strength KSI ASTM D-3410-87	Compressive Modulus MSI ASTM D-3410-87
Soy/E-Glass (2 plies)	0°	67.2	3.6	43.9	3.6
Dow PC-100 VE/E-Glass	0°	66.5	3.45	61	3.4
Soy/E-Glass	90°	46.7	3.0	26.2	3.0
Dow PC-100 VE/E-Glass	90°	47.0	2.55	49.2	2.6

The mechanical properties of the composite were determined and compared with those of a

commercial high performance vinylester resin (Dow PC-100) containing the same volume fraction of identical fibers. The above mechanical test data for the fiberglass composites provide a favorable comparison between commercial high performance composites and soyoil derived composite resins.

Example 43

100 g of acrylated epoxidized triglyceride was mixed with 45 g styrene, 5 g divinyl benzene, 2.25 g USP 245 free radical initiator. This liquid mixture was combined in an RTM with 30% wt of flax (Durafiber Grade 2, or, Mesh 10) fibers, randomly distributed, cured at 90 °C for 1 hour, followed by a postcure at 110 °C for 1 hour. The Mesh 10 flax consisted of flax shive with 2 mm average length; the Grade-2 flax fibers were decorticated fibers of much longer lengths. The resulting rigid composites with Durafiber Grade-2 flax had a tensile strength greater than 34 MPa and a tensile Young's modulus of 4.6 GPa. The specific gravity was 1.1. Water absorption tests (ASTM D570-81) on flax composites conditioned at 50 °C in a vacuum oven for 4 hours and allowed to cool to room temperature in a descicator for 30 minutes, gave the following results:

Table-Water Absorpti n Data for Flax Fiber C mposites

Flax Fiber 30% wt of Composite	Water Temperature	Immersion Time Hours	Weight Change %	Number of Samples Tested
Mesh-10 Shive	room	2	0.75	3
Mesh-10 Shive	Boiling	2	4.31	3
Grade-2 Fiber	room	2	1.27	3
Grade-2 Fiber	Boiling	2	5.43	3

Example 44

40 g of maleinized fatty acid monoglyceride and 40 g of acrylated epoxidized triglyceride were mixed with 30 g of styrene, 0.6 g dimethyl aniline and 0.8 g benzoyl peroxide. The mixture was degassed for 5 minutes by purging with nitrogen and injected into a mold. The mixture was heated at 90 °C for 1 hour and at 110 °C for 1 hour. The product was a rigid thermoset resin.

Example 45

110 g of acrylated epoxidized triglyceride was mixed with 45 g of styrene . 7.5 g of sulfur vulcanized soybean oil rubber resin was powdered at 0 °C and added to the mixture in Example 44 by high shear stirring. 1.5 g of USP 245 free radical initiator was added and the mixture was heated in a mold at 90 °C for 1 hour and at 110 °C for 1 hour. The product was a toughened rigid thermoset resin.

Example 46

45 g of acrylated epoxidized triglyceride was mixed with 1.5 g titanium isopropoxide and heated and stirred at 95 °C. The mixture became viscous in 40 minutes and gelled in 90 minutes and gave a rubbery polymer in 3 hours. This rubbery polymer was ground to a fine powder at 0 °C, washed twice with acetone and dried to give a resilient material. 1 g of the material was mixed with 12 g of acrylated epoxidized triglyceride and 8 g of styrene and 0.2 g of USP 245 free radical initiator. This mixture was heated at 90 °C for one hour and at 110 °C for 1 hour to give a toughened thermoset resin.

Example 47

100 g of acrylated epoxidized soyoil was mixed with 45 g of styrene. 5 g of divinyl benzene. 1.5 g of USP-245 Initiator and 7.5 g of vulcanized rapeseed oil rubber particles, commercially available from Harwick (Lot # C21185116). The rubber particle diameter was about 100 micrometers. The mixture was stirred to obtain a uniform dispersion of the rubber particles and the resin was cured at 90 °C for 1 hour and post cured at 110 oC for 1 hour. The resulting material was a rubber reinforced rigid solid with a Tg of 70 °C, as determined by DMA, a Young's modulus of 603 MPa and an Izod impact strength of 3.2 KJ/m^2. Izod fracture experiments were conducted on a Zwick Impact Tester Model 5113 using ASTM D 256-90b, test method-A. Scanning Electron Microscopy of the fracture surfaces from the Izod impact tests revealed that extensive crazes grew from the rubber particles normal to the principal stress direction, which is highly characteristic of a toughened glassy thermoset.

Example 48

30 g of maleinized triglyceride of Example 23 was mixed with 13 g of glycerolized triglyceride mixture from Example 26 and heated at 110 °C for 1 hour and at 130 °C for 2

hours. The product was a resilient rubber. The product was powdered at 0 °C and washed twice with acetone to give a resilient material. 1 g of this material was mixed with 12 g of maleinized fatty acid monoglyceride, 8 g styrene and 0.3 g USP 245 free radical initiator. The mixture was stirred at room temperature for 5 minutes until material particles were swollen and dispersed and then heated 1 hour at 90 °C and 1 hour at 110 °C in a mold. The product was a toughened rigid thermoset resin.

CLAIMS

We claim:

1. A process to produce a resin or composite which comprises the chemical modification of a saturated or an unsaturated plant oil so that chain extension and cross linking reactions can be induced to transform said plant oil into a rigid solid resin wherein said chemical modification is carried out by at least one of the following synthetic methods:

(a) ring opening polymerization,

(b) hydroxylation,

(c) maleinization,

(d) glycerolysis,

(e) amidation,

(f) modification of an acrylated epoxidized plant oil with at least one of the following groups:

(1) unsaturated anhydrides,

(2) saturated anhydrides,

(3) reactive diluents with diisocyanates and/or polyisocyanates,

(4) diamines,

(5) Lewis acids or

(6) alkoxides

(7) diacids

(g) free radical polymerization, or

(h) polycondensation.

2. A thermoset resin or composite which comprises a synthesized plant oil wherein said synthesis is carried out by at least one of the following methods:

(a) ring opening polymerization,
(b) hydroxylation,
(c) maleinization,
(d) glycerolysis,
(e) amidation,
(f) modification of an acrylated epoxidized plant oil with at least one of the following groups:
(1) unsaturated anhydrides,
(2) saturated anhydrides,
(3) reactive diluents with diisocyanates and/or polyisocyanates,
(4) diamines,
(5) Lewis acids or
(6) alkoxides
(7) diacids
(g) free radical polymerization or
(h) polycondensation.

3. The resin or composites as claimed in claim 2, wherein said synthesis is by the modification of an acrylated epoxidized triglyceride with at least one of the following groups:
(1) unsaturated anhydrides,
(2) saturated anhydrides,
(3) reactive diluents with diisocyanates and/or polyisocyanates,
(4) diamines,
(5) Lewis acids or
(6) alkoxides
(7) diacids

4. The process as claimed in claim 1, which comprises synthesizing by modification of an acrylated epoxidized triglyceride with at least one of the following groups:
(1) unsaturated anhydrides,
(2) saturated anhydrides,
(3) reactive diluents with diisocyanates and/or polyisocyanates,
(4) diamines,
(5) Lewis acids or
(6) alkoxides
(7) diacids

5. The resin or composites as claimed in claim 2, wherein said synthesis is by ring opening polymerization of epoxidized triglycerides with at least one of the following groups:
(1) diamines,
(2) dicarboxylic acids,
(3) dicarboxylic acid anhydrides,
(4) diols,
(5) polyols
(6) Lewis acids or
(7) alkoxides.

6. The process as claimed in claim 1, wherein said synthesis is by ring opening polymerization of epoxidized triglycerides with at least one of the following groups:
(1) diamines,
(2) dicarboxylic acids,
(3) dicarboxylic acid anhydrides,
(4) diols,
(5) polyols
(6) Lewis acids or
(7) alkoxides.

7. The resin or composite as claimed in claim 2, wherein said synthesis is by hydroxylation of triglyceride to form a polyol and said polyol is then subjected to maleinization.

8. The resin or composite as claimed in claim 2, wherein said triglyceride is an epoxidized triglyceride.

9. The process as claimed in claim 1, wherein said synthesis is by hydroxylation of triglycerides to form a polyol and said polyol is then subjected to maleinization.

10. The process as claimed in claim 9, where said triglyceride is an epoxidized triglyceride.

11. The resin or composite as claimed in claim 2, wherein said synthesis is by reaction of a hydroxylated triglyceride with an epoxy resin and an ethylenically unsaturated anhydride.

12. The process as claimed in claim 1, wherein said synthesis is by reaction of a hydroxylated triglyceride with an epoxy resin and an ethylenically unsaturated anhydride.

13. The resin or composite as claimed in claim 2, wherein said synthesis is by maleinization of a triglyceride to form a resulting polyanhydride and polymerization of the resulting polyanhydride with at least one of the groups
(a) diamines,
(b) diols and/or polyols or
(c) epoxide.

14. The process as claimed in claim 1, wherein said synthesis is by maleinization of a triglyceride to form a resulting polyanhydride and then polymerizing the resulting polyanhydride with at least one of the groups
(a) diamines,
(b) diols and/or polyols or
(c) epoxide.

15. The resin and composite as claimed in claim 2, wherein said synthesis is by glycerolysis of a triglyceride to form a resulting polyol and said resulting polyol is then subjected to maleinization.

16. The process as claimed in claim 1, wherein said synthesis is by glycerolysis of a triglyceride to form a resulting polyol and said resulting polyol is then subjected to maleinization

17. The resin and composite as claimed in claim 2, wherein said synthesis comprises the steps of
(a) glycerolysis of a triglyceride,
(b) hydroxylation to form a resulting polyol and
(c) maleinization of said resulting polyol.

18. The process as claimed in claim 1, wherein said synthesis comprises the steps of
(a) glycerolysis of a triglyceride,
(b) hydroxylation to form a resulting polyol and
(c) maleinization of said resulting polyol.

19. The resin and composite as claimed in claim 2, wherein said synthesis is by glycerolysis of a triglyceride to form a resulting polyol, following by polymerization of said resulting polyol with di-isocyanates and poly isocyanates.

20. The process as claimed in claim 1, where said synthesis is by glycerolysis of a triglyceride to form a resulting polyol, followed by polymerization of said resulting polyol with diisocyanates and poly isocyanates.

21. The resin or composite as claimed in claim 2, wherein said synthesis is by amidation of a triglyceride with a hydroxy amine to form a resulting polyol and then maleinization of said resulting polyol.

22. The process as claimed in claim 1, wherein said synthesis is by amidation of a triglyceride with a hydroxy amine to form a resulting polyol and then maleinization of said resulting polyol.

23. The resin or composite as claimed in claim 2, wherein said synthesis is by amidation of a triglyceride with a polyamine to form a resulting polyamine and then polymerizing said resulting polyamine with epoxy resin.

24. The process as claimed in claim 1, wherein said synthesis is by amidation of a triglyceride with a polyamine to form a resulting polyamine and then polymerizing said resulting polyamine with epoxy resin.

25. A thermoset resin or composite mixture which comprises at least two different resins, with at least one of said resins being said resin as claimed in claim 2.

26. The resin or composite as claimed in claim 2, which further comprises an admixture of at least one elastomeric toughening agent.

27. The resin or composite as claimed in claim 2, which further comprises the resin or composite is reinforced with at least a reinforcing member which is selected from the group consisting of glass, carbon, aramid, boron, silicone carbide, man made fibers and natural fibers.

28. The thermoset composite as claimed in claim 27, wherein said reinforcing member is an animal fiber, plant fiber or vegetable fiber.

29. The thermoset composite as claimed in claim 28, wherein said animal fiber is wool, cashmere, hair or bird feathers.

30. The thermoset composite as claimed in claim 28, wherein said plant fiber or said vegetable fiber is cotton, sisal, fibrous cellulose, hemp, hay, straw, flax, jute, or pine needles.

31. A process to produce a polymer or composite which comprises reacting the resin as claimed in claim 2, by Resin Transfer Molding (RTM), Reaction Injection Molding (RIM), Vacuum Assisted Resin Transfer Molding (VARTM), Seeman's Composite Resin Infusion Manufacturing Process (SCRIMP), Atmospheric Pressure Molding (APM), open mold casting, spray-up, Sheet Molding Compound (SMC), Bulk Molding Compound (BMC), Particle Board Pressing, Oriented Fiber Strand Pressing, filament winding, pultrusion, fiber placement or prepreg formation.

32. A polymer or composite produced by the process as claimed in claim 31

33. A method which comprises utilizing the polymer as claimed in claim 32, as an application for civil infrastructure, defense materiel, aerospace, civil aeronautics, marine offshore/inshore, housing and building construction, particle board, automotive, rail transportation carriages and wagons, trucks and buses, agricultural equipment, sculpture, furniture and sporting goods and equipment.

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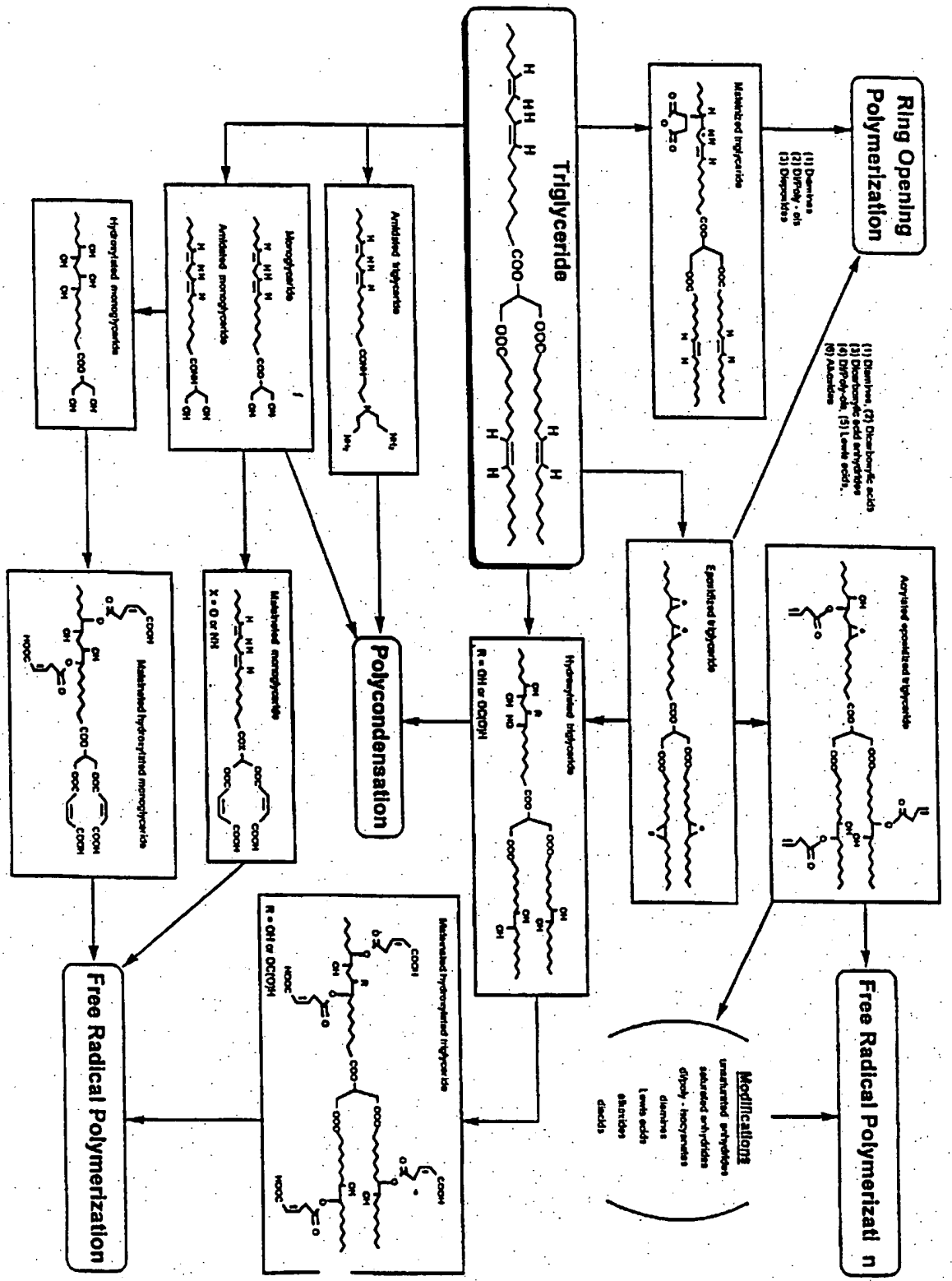
Ring Opening Polymerization
Triglyceride
Maleinized triglyceride
(1) Diamines
(2) Di/Poly - ols
(3) Diepoxides
(1) Diamines, (2) Dicarboxylic acids
(3) Dicarboxylic acid anhydrides
(4) Di/Poly-ols, (5) Lewis acids,
(6) Alkoxides
Epoxidized triglyceride
Acrylated epoxidized triglyceride
Free Radical Polymerization
Modifications
unsaturated anhydrides
saturated anhydrides
di/poly - isocyanates
diamines
Lewis acids
alkoxides
diacids
Hydroxylated triglyceride
R = OH or OCOOH
Polycondensation
Amidated triglyceride
Monoglyceride
Amidated monoglyceride
Hydroxylated monoglyceride
Maleinized monoglyceride
X = O or NH
Maleinized hydroxylated monoglyceride
Maleinized hydroxylated triglyceride
Free Radical Polymerization

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/22095

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :C08F 22/10; C08G 63/48
US CL :526/321; 528/295.5
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 526/321; 528/295.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,983,716 A (RAO et al.) 08 January 1991, columns 2-4.	1-33
X	US 5,506,285 A (TIMM et al.) 09 April 1996, column 8.	1-33
X	US 5,602,265 A (VAN DEN KOMMER et al.) 11 February 1997, columns 4-5.	1-33

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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03 FEBRUARY 1999	22 FEB 1999
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